



EVALUATION OF HEAVY METAL CONCENTRATION AND POLLUTION INDEX IN DUST SAMPLES IN KADUNA METROPOLIS

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ABSTRACT

Air pollution status has undergone changes in the levels of pollutants and control measures to reduce them. This study aimed at evaluating the heavy metal concentration and pollution index in dust samples in Kaduna metropolis. Dust samples were collected from the atmosphere using well improvised polythene bags from Nigerian Bottling Company (NBL), KASUPDA, Stadium roundabout, Secretariat and Millennium City. Samples were analyzed for Pb, Cu, Zn, Cd, Co, Fe, Mn and Ni and for pollution index (enrichment factor, geo-accumulation index, contamination factor and degree of contamination). Heavy metal concentration result showed significant difference ($p \leq 0.05$) in the different locations examined. All the metals analyzed recorded the highest concentration in KASUPDA > NBL > Stadium roundabout > Secretariat > Millennium city. The enrichment of the heavy metals showed minimally to moderately enriched in all study sites, ranging from 10.36 - 20.30. Cadmium was anomalously enriched in all the study sites, ranging from 700.71-1000. All heavy metals were in the range of unpolluted to moderately polluted (0.00-2.77) except for Cd which was strongly polluted with the range of 0.01 - 4.17. Pb, Cu, Zn, Co, Fe, Mn and Ni had low contamination factors and ranged from 0.01 - 0.40 except Cd which showed very high contamination factor (13.82 - 20.78). The degree of contamination (C_{deg}) for each site showed range of moderate to considerable degree of contamination (14.12 - 21.93). KASUPDA recorded the highest value of 21.93, though, with considerable degree of contamination. Conclusively, contamination of air and air pollution by heavy metals is more pronounced in the industrial areas of Kaduna which can be checked through government policies and the use of modern equipments to minimize the pollution.

Keywords: AAS, Air pollution, Enrichment factor, Geo-accumulation Index, Heavy metal, Kaduna metropolis, Pollution index

INTRODUCTION

Pollution refers to the contamination of the earth's environment with materials that interfere with human health, quality of life or the natural functioning of the ecosystems (Brook *et al.*, 2003). According to the World Health Organization, around two million people die prematurely from the effects of polluted air every single year (WHO, 2004). Air pollution is a huge problem not just for people living in smog-choked cities, but also through global warming and damage to the ozone layer which has the potential posing deleterious effects. Air pollution is a major problem faced globally and mainly arising from industrialization, unplanned urbanization, increase in vehicular fleet and population growth (Kaler *et al.*, 2016). With rapid development of human civilization and subsequent increased number of automobiles, air quality ultimately deteriorates. Motor vehicles account for 60-70% of the pollution found in urban environment (Verma & Chandra, 2014). Globally, urban air pollution is a major concern, with air pollution growing with negative impacts on human health. Respiratory health diseases and social inequality have increased due to air pollution (Addis, 2023; Sunyer *et al.*, 2021, Wang *et al.*, 2021).

Heavy metals commonly refer to a group of comparatively dense and harmful elements, even in very low concentrations (Appenroth, 2010). Such group of elements comprise metals and metalloids which possess densities higher than 5 g cm^{-3} and atomic mass varying from 60 to 200 g mol^{-1} (Burakov *et al.*, 2018; Barakat, 2011). Arsenic (As), chromium (Cr),

cadmium (Cd) and copper (Cu) are few of heavy metals present in different ecosystems and wastewater, with levels varying typically from nanogram liter⁻¹ to milligram liter⁻¹ (Fu *et al.*, 2017; Singh *et al.*, 2015; Kim *et al.*, 2013). Heavy metals can pose serious health challenges when they find their way into the body system. Consumption of heavy metal contaminated food can seriously deplete some essential nutrients in the body that are further responsible for decreasing immunological defenses, intrauterine growth retardation, disabilities associated with malnutrition and high prevalence of upper gastrointestinal cancer rates (Khan *et al.*, 2008).

Enrichment assessment of samples is one of the key components of determining the pollution indices of a sample. Environmental assessment of pollution indices uses indicators such as enrichment factor, geo-accumulation index, contamination factor and degree of contamination (Abraham and Parker, 2008). Enrichment factor (EF) is the minimum factor by which the weight percent of minerals in an ore body is greater than the average occurrence of that mineral in the earth's crust. Enrichment factor is a powerful tool to distinguish between anthropogenic and naturally occurring sources of heavy metals. Enrichment factor technique is used in the area of atmospheric aerosols, sediments, soil and solid wastes to determine the degree of modification in the composition (Feng, 2011). A common approach to estimating the enrichment of metal concentrations above background or baseline concentrations

is to calculate the geo-accumulation index (*I_{geo}*) as proposed by Müller, 1969 (Likuku *et al.*, 2013).

MATERIALS AND METHODS

Dust Sample Collection and Preparation

Dust samples were randomly collected from NBL, KASUPDA, Stadium Roundabout, Secretariat and Millennium City in Kaduna metropolis which served as the selected industrial, commercial and control sites during the dry season of 2022. A well labelled improvised polythene bag was used to collect dust samples directly from the atmosphere by suspending the polythene bags in improvised staking sticks at a height of 2 meters, without any interference, and also from leaf surfaces. The collected samples were kept in the polythene bags and transported to the laboratory. The dust was sieved with a 2 µm sieve net using the method described by Molnar (2016).

Determination of Dust pH

Exactly 1.0 g of dried dust sample from each site was mixed with 20 cm³ of deionized water in a 50 cm³ beaker and stirred with a glass rod. The pH was measured by introducing the probe of the pH meter (Model: HS-2CB) into the dust solution and the readings recorded.

Total Metal Analysis

Exactly 1.0 g of the dried dust sieved sample was weighed into a 100 cm³ beaker (pyrex), and digested with a mixture of 3 cm³ concentrated HNO₃ and 2 cm³ of HClO₄ for 1 hour at 100 °C in a fume cupboard. After cooling, the mixture was filtered and made up to 50 cm³ volume with deionized water. It was analyzed using Atomic Absorption Spectrophotometer (Model: AA-6800) and the results reported in parts per million (ppm).

Evaluation of Pollution Indices

Enrichment Factor (EF)

Enrichment factor (EF) of metals were calculated as:

$$EF = (X_{aerosol} / X_{refaerosol}) / (X_{ucc} / X_{refucc})$$

where X is the element under consideration both in aerosol and the upper continental crust (ucc) and Ref is a reference element that is typically crystal such as Al, Fe, Li, Ti etc. Metal abundances in UCC given in Wedepohl (1995) were used and Fe was chosen as the reference metal. Five contamination categories are recognized on the basis of the enrichment factor: EF < 2 states deficiency to minimal enrichment, EF = 2-5 moderate enrichment, EF = 5-20 significant enrichment, EF = 20-40 very high enrichment and EF > 40 extremely high enrichment (Feng, 2011).

Geo-accumulation Index

This was calculated using the equation:

$$I_{geo} = \text{Log}_2 (C_n / 1.5B_n)$$

where *C_n* is the measured concentration of the element, *n* and *B_n* is the geo-chemical background value element “*n*” in average crust (Wedepohl, 1995). The factor 1.5 is used to compare possible variations which may be attributed to lithologic variations in the sediment (Lu *et al.*, 2009).

Contamination Factor and Degree of Contamination (C_{deg})

This is a single element index which is determined by the relation:

$$C_f^i = \frac{C_{0-1}^i}{C_n^i}$$

where *C_fⁱ* is the contamination factor of the element of interest, *C₀₋₁ⁱ* is the concentration of the element in the sample, *C_nⁱ* is the background concentration. The sum of the contamination factors of all the elements in the sample gives the degree of contamination as indicated in the equation below: Total Heavy Metal Concentration in Dust Samples.

$$\sum C_{deg}^i = C_f^i$$

Statistical Analysis

Results obtained were expressed as mean (±) standard deviation of mean with three replicates for each of the parameter measured. Statistical Package for Social Sciences (SPSS) Version 23 was used for the data analyses. Data generated for each of the parameters were subjected to one way Analysis of Variance (ANOVA), using Completely Randomized Design (CRD). Tukey test was used for the separation of means where significant difference of *p* < 0.05 occurred.

RESULTS AND DISCUSSION

Results

Heavy Metal Concentration in Dust Samples

The result of the heavy metal concentration of the selected locations in Kaduna Metropolis showed that significant difference (*p* ≤ 0.05) occurred in the concentration of the heavy metals examined (Table 1). It was observed in the result that among the heavy metals analyzed (Pb, Cu, Zn, Cd, Co, Fe, Mn and Ni) recorded the highest concentration in KASUPDA followed by NBL, Stadium roundabout, Secretariat and Millennium city. No significant difference was however, observed in the Pb concentration between SR and SEC. Copper concentration between NBL, SR and SEC, with similar trends across all the metals (Table). All the metals were observed to be within the WHO limit except for cadmium as observed in all the locations.

Table 1: Concentration of heavy metals in NBL, KASUPDA, Stadium Roundabout, Secretariat and Millennium City in Kaduna Metropolis

Metal	Average concentration of metals in dust samples (mg/kg)					WHO Limit (mg/kg)
	NBL	KASUPDA	SR	SEC	MILL (Control)	
Pb	2.15±0.06 ^b	3.75±0.08 ^a	1.40±0.18 ^c	1.18±0.25 ^c	0.35±0.01 ^d	2-200
Cu	0.93±0.01 ^b	3.03±0.02 ^a	0.96±0.01 ^b	0.80±0.03 ^b	0.33±0.04 ^c	2-100
Zn	14.72±0.00 ^b	20.81±0.01 ^a	15.67±0.01 ^b	12.01±1.00 ^{bc}	10.74±0.01 ^c	50-300
Cd	1.66±0.01 ^b	2.12±0.00 ^a	1.90±0.01 ^a	1.90±0.01 ^a	1.41±0.03 ^c	0.01-0.7
Co	1.78±0.03 ^b	2.67±0.03 ^a	1.66±0.02 ^b	0.27±0.03 ^c	0.09±0.04 ^d	24-100
Fe	884.7±0.89 ^b	1133.80±0.00 ^a	805.12±0.72 ^b	1107.22±0.16 ^a	609.77±0.25 ^c	7000-550,000
Mn	6.46±0.22 ^b	8.55±0.01 ^{ab}	6.72±0.00 ^b	11.55±0.21 ^a	3.74±0.18 ^c	20-3000
Ni	0.44±0.01 ^b	0.66±0.01 ^a	0.40±0.02 ^b	0.60±0.01 ^a	0.34±0.01 ^c	5-500

NBL = Nigerian Bottling Company, SR = Stadium Roundabout, SEC = Secretariat, KAP = KASUPDA, MILL = Millennium City

Metal Enrichment in the Dust Samples

The enrichment of the heavy metals in the dust samples were minimally to moderately enriched in all the study sites and

ranged from 10.36-20.30 (Table 2). Cadmium was anomalously enriched in the dust samples throughout all the study sites ranging from 700.71-1000.

Table 2: Heavy Metal Enrichment in the Dust Samples

Metals	NBL	KAP	S/R	SEC	MIL
Pb	5.87	10.20	3.83	3.23	0.96
Cu	1.51	9.94	3.15	2.62	1.08
Zn	14.25	20.08	15.12	11.59	10.36
Cd	824.95	1053.55	994.22	994.22	700.71
Co	7.47	11.52	7.16	1.17	0.39
Fe	1.45	1.86	1.32	1.82	1.00
Mn	0.62	0.82	0.65	1.11	0.36
Ni	1.20	1.82	1.09	1.64	0.93

NBL =Nigerian Bottling Company, S/R = Stadium Roundabout, SEC = Secretariat, KAP= KASUPDA, MILL = Millennium City.

Key = EF = 2 – 5 Moderate Enrichment; 5 – 20 Significant Enrichment; 20 – 40 Very High Enrichment; > 40 Extremely Enrichment

Geo-accumulation Index of the Heavy Metals in Dust Samples

The result of the geo-accumulation index showed that the values for Pb, Cu, Zn, Co, Fe, Mn and Ni were all in the range

of unpolluted to moderately polluted (0.00 - 2.77) except for Cd which was strongly polluted with the range of 0.01 - 4.17 across the study sites (Table 3).

Table 3: Evaluation of the Geoaccumulation Index (Igeo) of the Heavy Metals in the Dust samples

Metals	NBL	KAP	S/R	SEC	MILL (control)
Pb	0.03	0.04	0.02	0.01	0
Cu	0.01	0.04	0.01	0.01	0.04
Zn	0.06	0.08	0.06	0.05	2.77
Cd	3.27	4.17	3.74	3.74	0.01
Co	0.03	0.05	0.02	0.01	0
Fe	0.01	0.01	0.01	0.01	0
Mn	0	0	0	0	0
Ni	0	0.01	0	0.01	0

NBL = Nigerian Bottling Company, S/R = Stadium Roundabout, SEC = Secretariat, KAP = KASUPDA, MILL = Millennium City.

Key = I_{geo} = < 0 = practically unpolluted; 0-1= unpolluted to moderately polluted; - 2 = moderately polluted; 2-3 = moderately to strongly polluted, 3-4 = strongly polluted, 4-5 = strongly to extremely Polluted; > = extremely polluted

Contamination Factor and Degree of Contamination (Cdeg) of the Heavy Metals in the Dust Samples

The result of the contamination factor and degree of contamination showed that Pb, Cu, Zn, Co, Fe, Mn and Ni had low contamination factor observed to be between range of 0.01 - 0.40 except for Cd which showed very high

contamination factor (13.82 - 20.78) (Table 4). The degree of contamination (C_{deg}), for each experimental location showed moderate degree of contamination to considerable degree of contamination (14.12 - 21.93). KASUPDA recorded the highest value of 21.93 though with considerably degree of contamination (Table 4).

Table 4: Evaluation of Contamination Factor and Degree of Contamination (Cdeg) of the Heavy Metals in the Dust Samples.

Metals	NBL	KAP	S/R	SEC	MIL
Pb	0.13	0.22	0.08	0.06	0.02
Cu	0.07	0.21	0.07	0.06	0.02
Zn	0.28	0.4	0.3	0.23	0.21
Cd	16.27	20.78	18.63	18.63	13.82
Co	0.15	0.24	0.14	0.02	0.01
Fe	0.03	0.04	0.02	0.04	0.01
Mn	0.01	0.02	0.01	0.02	0.01
Ni	0.02	0.02	0.02	0.03	0.02
(C _{deg})	16.96	21.93	19.27	19.09	14.12

NBL = Nigerian Bottling Company, S/R = Stadium Roundabout, SEC = Secretariat, KAP= Kasupda, MILL = Millennium City.

Key = C_{deg} > 1 = Low contamination factor, 1 - 3 = moderately contamination, 3 - 6 = considerable contamination factor, > 6 = very high contamination

Principal Component Analysis

The rotated component matrix for the principal component analysis is presented in Table 5. The result of the varimax rotation with Kaiser Normalization gave three components accounting for 98.3% of the cumulative variance. Component 1 has moderate low factor loadings for Pb, Cu, Cd, Co, Ni, Fe,

Zn (0.323 - 0.380) accounting for 74.1% variance. Component 2 was dominated by Mn and low factor loadings for Fe (0.350), while Ni (0.338) accounted for 21.4% variance. Component 3 accounted for 2.9% of the total variance while Cd occurred as the major component (0.564).

Table 5: Principal Component Analysis (Rotated Component Matrix)

Variable	PC 1	PC 2	PC 3
Pb	0.382	-0.238	-0.234
Cu	0.380	-0.203	-0.446
Zn	0.365	-0.345	0.120
Cd	0.385	0.100	0.564
Co	0.323	-0.440	0.350
Fe	0.361	0.350	-0.095
Mn	0.257	0.585	0.298
Ni	0.358	0.338	-0.439
Eigenvalue	5.925	1.720	0.229
% Variance	74.100	21.400	2.900
% Cumulative	74.100	95.400	98.300

Discussion

The high copper concentration observed in this research work might be from weathering activities and construction works which might have been washed to the sample location by erosions. Although, copper is an essential trace element to human life as it assists important enzymes to function effectively and also plays a role in the production of haemoglobin, myelin and melanin in the body (Mustafa and AlSharif, 2018). When it occurs in high doses, it causes anemia, liver and kidney damage, stomach and intestinal irritation (Taylor *et al.*, 2020). The range of values for zinc as observed in this research work is higher than those reported by Atiemo *et al.* (2011); Omaka *et al.* (2013) in dust samples. However, the mean values reported in the different sites are lower than the WHO value of 50 mg/kg of Zn in the soil. The high concentration reported in KASUPDA may be related to atmospheric deposition and industrial waste discharge. Zinc concentration might also be from mechanical abrasion of vehicles and from zinc compounds used extensively as antioxidants (e.g Zinc carboxylate complexes and sulphates) as detergents dispersant improves for lubricating oils which also agreed with the report of Monika and Romic (2011).

The cadmium concentration ranged from 0.81-2.12 mg/kg with the highest value recorded in KASUPDA. The exceedingly higher concentration in KASUPDA might be due to the presence of cadmium in automobile fuel due to the mechanic workshop station in the location. Omaka *et al.* (2014) recorded a lower value of 0.001 mg/kg in dust sample for Cd compared to the mean value of 1.80 mg/kg recorded in this study. This value was higher than the value of 0.7 mg/kg for WHO standard for heavy metal in soil. The value of Cobalt in the study site ranged from 0.09-2.69 mg/kg with KASUPDA recording the highest value of 2.67 mg/kg, followed by NBL, S/R and Secretariat. Similar work reported the range of 11.16 - 1544.24 ppm for Cobalt (Sana`a, 2013). This concentration value was very high compared to the mean value of 2.67 mg/kg reported in this study.

The high concentration of Fe in KASUPDA may be attributed to the fact that it is located near a motor garage by the road side and close to a vulcanizer workshop. The activity in the motor garage and repairs by the vulcanizer may have contributed to the high Fe content in this site. The value of 6.54 ppm was reported in literature for Fe in dust samples carried out in Ebonyi state (Omaka *et al.*, 2013). Concentration of Mn in dust sample ranged from 3.74-11.55

mg/kg with the highest value recorded in Secretariat followed by KASUPDA. The mean value of 7.40 mg/kg of Mn recorded in the study was lower than the WHO value of 20 mg/kg for heavy metal concentration in soil. Mufiyai *et al.* (2014) reported the value of 0.002-0.058 mg/kg for Mn. Mn is an essential element but very high concentration of it in respirable dust can be dangerous to human health. The high concentration value of Mn may be attributed to anthropogenic activities such as coal fires and tyre wear.

The concentration of Ni ranges from 0.34-0.66 mg/kg with a mean value of 0.48 mg/kg. Site 2 (KASUPDA) recorded the highest concentration followed by Secretariat. These sites are prone to high traffic congestion. The high concentration of Nickel may be due to anthropogenic activities that emit Ni into the air such as combustion of fuel and residual oil, mining, municipal waste incineration and the high rate of old vehicles plying the road. The mean range of 3.74 - 11.78 mg/kg in this work is higher the range of 0.021-0.216 mg/kg reported by Mafuyai *et al.* (2014) and lower than the value of 124.52 mg/kg reported in Accra for roadside dust (Atiemo *et al.*, 2011) which is lower than the WHO permissible limit of 5-500 mg/kg.

The enrichment factor for Pb obtained from all the sites ranged from 0.96 - 10.20 which indicated that the element is significantly enriched in the dust. Pb was for a long time used as an octane enhancer until it was phased out in 2004. The Pb residues around the locations and the wearing of mechanical materials made of lead might have been the source of the lead concentration in the dust samples. The Pb enrichment result in this work is similar to the one reported by Atiemo *et al.*, (2011). Cu showed minimal enrichment in NBL and Millennium City, moderate in Stadium roundabout and Secretariat and significant enrichment in KASUPDA while the enrichment of Zn was also significant, ranging between 10.36 to 20.08 in the locations assessed. The high enrichment obtained in all the sites may probably be due to traffic congestion and significant tyre abrasion. The enrichment of Cd ranged from 700.71 - 1000 which indicates that the element is anomalously enriched in the dust. This is in agreement with published literature as all the elements belonging to this group have a known crustal source in addition to various emission sources (Salvador *et al.*, 2004). Similar studies on inhalation metals revealed enrichment of cadmium in the range of 100 - 1000 (Khilare and Sarkar, 2012). Vehicular tire wear, battery- manufacture, pigments,

metal plating and smelting industries are important sources of these metals (Querol *et al.*, 2007).

The result of the geo-accumulation index showed that the value for Pb, Cu, Zn, Co, Fe, Mn and Ni are all in the range of unpolluted to moderately polluted (0.00 – 2.77) except for Cd which is strongly polluted with the range of 0.01 – 4.17. The most likely source of the Cd might have been vehicular emissions, similar to the reported work by Lu *et al.* (2009). The exceedingly high Cd contamination factor when compared to the other metals agrees with the enrichment factor and geo-accumulation index that showed that Cd was anomalously enriched in the dust samples. The degree of contamination (C_{deg}), computed for each site showed moderate to considerable degree of contamination (14.12 - 21.93). KASUPDA showed the highest value of 21.93, though, with considerable degree of contamination.

In this study, all principal factors extracted from the variables were retained with eigen values > 1.0, as suggested by the Kaiser criterion (Kaiser, 1960). Principal component 1 is likely to be of natural crust origin. Pb, Cu, Cd, Co, Ni, Fe, Zn showed low to moderate enrichment giving indication of crustal origin (Shridhar *et al.*, 2010). The high value expressed by manganese in component 2 could be due to the resuspension of road dust by vehicular turbulence. So, this factor represents vehicular sources. Mn had low to moderate enrichment factor, unpolluted to moderately polluted and with a low contamination factor indicating industrial and vehicular emission sources as reported by Querol *et al.* (2007). The enrichment factor, geoaccumulation factor and contamination factor obtained for Cd shows that it is anomalously enriched and strongly contaminated giving an indication of anthropogenic origin (Okunola *et al.*, 2008). This might be responsible for its high component 3 value.

CONCLUSION

The selected heavy metals (Pb, Zn, Cu, Cd, Ni, Mn, Fe, and Co) were all detected in the total metal analysis of the dust samples using AAS with Fe recording the highest value of 1133.80 ppm and Nickel the least. Enrichment factor, geo-accumulation index, contamination factor and degree of contamination calculated showed that Cadmium (Cd) was anomalously enriched, strongly polluted and with a high contamination factor. Pb, Zn, Cu, Ni, Mn, Fe, and Co were minimally to significantly enriched, unpolluted to minimally polluted and with a low contamination factor.

Principal Component Analysis (PCA) gave three components which are natural crust, vehicular emissions, corrosion and wear of vehicle parts. Component 1 has moderate low factor loadings for Pb, Cu, Cd, Co, Ni, Fe, and Zn accounting for 74.1% variance indicating natural crust origin. Component 2 was dominated by Mn and low factor loadings for Fe and Ni accounting for 21.4% variance. This factor represents vehicular sources. Component 3 accounts for 2.9% of the total variance and has Cd as the major component. The enrichment factor, geo-accumulation factor and contamination factor obtained for Cd shows that Cd is anomalously enriched and strongly contaminated giving an indication of anthropogenic origin.

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